

POLYMER-BASED FORMULATION FOR TEXTILE RINSING

The present invention relates to an improved formulation intended for the rinsing of textile fiber articles, comprising an active substance comprising a particulate solid organic polymer; it likewise relates to a method of enhancing the antiwrinkle properties and/or easy-iron properties and/or soil release properties of textile fiber articles by contacting said articles with said improved formulation in the course of a rinsing operation.

The use, in compositions for treating textile fiber articles in aqueous medium, of insoluble particles of organic polymers or of aqueous dispersions of insoluble particles of organic copolymers has already been described (US-A-3,340,217).

Polymer dispersions have been claimed in washing compositions for conferring antifelting properties (US-A-4,746,455).

Dispersions of alkali-soluble polymers have been proposed for enhancing the removal of soiling (EP-A-279 134).

The use, in compositions for treating laundry in an aqueous or damp medium (formulations for washing, rinsing and/or softening, drying, ironing, prespotting), of nanoparticles or of aqueous dispersions of nanoparticles of insoluble polymer or copolymer as antiwrinkle and/or easy-iron agents is

described in WO 02/18451.

Moreover, the use of polymer particles as a reservoir containing fragrances or an active detergent substance has already been described in WO 99/38944 and

5 WO 01/46357.

It has been found that the adsorption thus obtained of this type of compound on the textile surfaces is insufficient to provide any notable benefit to the surfaces thus treated.

10 The Applicant has now found that the addition, to a formulation comprising insoluble organic particles of polymer and intended for the rinsing of textile fiber articles, of a small amount of an appropriately selected soluble vehicle for said polymer
15 makes it possible to improve significantly the deposition of particles on the surface of said articles and hence to confer notable benefits on said articles, in particular antiwrinkle properties and/or easy-iron properties and/or soil release properties.

20 The invention first provides a formulation (F) intended for use in an operation of rinsing (R) textile fiber articles (S) by means of an aqueous or aqueous-alcoholic medium (MR), said formulation (F)
- comprising at least one active substance (A)
25 comprising a solid organic polymer in particulate form and a vehicle (V) comprising at least one organic polymer, capable of taking said active substance (A) to

the surface of said textile fiber articles (S) in the rinsing operation (R),

- in the form:

- of a stable dispersion, with a pH of from 2 to 5, of said active substance (A) in an aqueous or aqueous-alcoholic medium (MAV) comprising said vehicle (V), or
- in a solid form obtained by drying said dispersion,

10 the nature of the active substance (A), of the aqueous or aqueous-alcoholic medium (MAV), and of the vehicle (V) being such that

* the active substance (A)

- is insoluble in the medium (MAV),
- 15 • has an overall zero or cationic charge in the medium (MAV),
- is stabilized in the medium (MAV) by means of a cationic surfactant (TAC), it being possible for said cationic surfactant
- 20 (TAC) to be wholly or partly replaced by a nonionic surfactant when the polymer constituting the active substance (A) is intrinsically cationic or intrinsically potentially cationic in the medium (MAV),
- 25 • remains insoluble in the rinsing medium (MR) or is capable of swelling in the rinsing medium (MR);

- * the vehicle (V)
- is soluble or dispersible in the medium (MAV) and in the rinsing medium (MR)
 - has an overall cationic or zero ionic charge in the medium (MAV),
 - at the pH of the rinsing operation in the rinsing medium (MR) is capable of developing anionic charges in sufficient quantity to destabilize the active substance (A) in the rinsing medium (MR).

The formulation according to the invention is intended for use equally for implementing a washing machine rinsing operation as a hand rinsing operation. This operation is commonly carried out at a pH which can range from 5.5 to 8 (pH of the supply circuit water); it usually takes place at ambient temperature. In a conventional laundry washing operation, the rinsing formulation is employed in the final rinse.

A particle dispersion is considered as being stable if no sedimentation, phase separation or development of turbidity is observed over time. This dispersion is destabilized when the particles undergo aggregation with one another.

According to the invention the active substance (A) is considered as being destabilized in the rinsing medium (MR) comprising the vehicle (V) when the turbidity of said medium is at least 5 times greater than the

turbidity which the same medium would have in the absence of vehicle (V).

According to the invention the active substance (A) is in a solid or liquid organic or organosilicon material in particulate form which is insoluble in the medium (MAV), has an overall zero or cationic charge in the medium (MAV), remains insoluble in the rinsing medium (MR) or is capable of swelling in the rinsing medium (MR).

10 The term "polymer" is used here to denote both a homopolymer and a copolymer. The term copolymer will be used when the polymer in question is derived from at least two monomers of different type.

 Among the polymers which may form the active substance (A) mention may be made of the following:

- 15 a) nonionic polymers derived from at least one nonionic hydrophobic monomer
- b) copolymers derived from at least one nonionic hydrophobic monomer and at least one monomer which is cationic or potentially cationic in the medium (MAV), and optionally at least one monomer which is neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR)
- 20 c) copolymers derived from at least one nonionic hydrophobic monomer and at least one monomer which is neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR).

The monomer composition from which said polymer is derived may further comprise

- 5 - at least one noncharged or nonionizable hydrophilic monomer, preferably in an amount not exceeding 50% of the total mass of the monomers
- and/or at least one zwitterionic monomer, preferably in an amount not exceeding 30% of the total mass of the monomers,
- 10 - and/or at least one crosslinking monomer, preferably in an amount not exceeding 10% of the total mass of the monomers.

When the polymers in question are copolymers b) above, the monomer composition from which said
15 copolymers are derived may optionally further comprise a small amount of anionic monomer whose first pKa is less than 3, although the copolymer b) must have a cationic overall charge in the medium (MAV).

When the polymers in question are ionic or
20 ionizable copolymers, the selection and relative amounts of monomers from which said copolymers are derived are such that the active substance (A)

- is insoluble in the medium (MAV)
- exhibits a zero or cationic overall charge
- 25 in (MAV)
- remains insoluble in the rinsing medium (MR) or is incapable of swelling by more than 8 times,

preferably not more than 4 times, its volume in the rinsing medium (MR).

Accordingly

- when a monomer which is neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR) is present in the monomer composition it preferably represents not more than 50% of the total mass of the monomers, so that the resulting copolymer does not swell by more than 8 times, preferably not more than 4 times, its volume in the rinsing medium (MR);
- when an anionic monomer (whose first pKa is less than 3) is present in the monomer composition, it preferably does not represent more than 20%, more particularly not more than 10%, of the total mass of the monomers, so that said copolymer has a cationic overall charge in the medium (MAV)
- when a zwitterionic monomer is present in the monomer composition, it preferably does not represent more than 30%, with preference not more than 20%, of the total mass of the monomers, so that said copolymer has a cationic overall charge in the medium (MAV).

Said polymer constituting the active substance (A) is in particulate solid form. Said particles may have an average diameter ranging from 10 nm to 10 μ m, preferably from 10 nm to 1 μ m, and more

preferably from 10 nm to 500 nm.

The diameter of said particles may be determined in well-known manner by light scattering or by transmission electron microscopy.

5 Preferentially, the monomers from which the polymers constituting the active substances (A) are derived are α - β monoethylenically unsaturated or diethylenically unsaturated in the case of the crosslinking monomers.

10 By way of examples of hydrophobic nonionic monomers mention may be made of

- vinylaromatic monomers such as styrene, vinyltoluene, etc.
- alkyl esters of α - β monoethylenically unsaturated acids, such as methyl acrylates and methacrylates, ethyl acrylates and methacrylates, etc.
- vinyl or allyl esters of saturated carboxylic acids, such as vinyl or allyl acetates, propionates, and versatates
- 20 • α - β monoethylenically unsaturated nitriles such as acrylonitrile, etc.
- α -olefins such as ethylene, etc.

By way of examples of cationic hydrophilic monomers mention may be made of

- 25 • acryloyl- or acryloyloxammonium monomers such as trimethylammoniumpropyl methacrylate chloride, trimethylammoniummethacrylamide or -methacrylamide

- chloride or bromide, trimethylammoniumbutylacrylamide or -methacrylamide methyl sulfate, trimethylammoniumpropylmethacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyltrimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride;
- 1-ethyl-2-vinylpyridinium or 1-ethyl-4-vinylpyridinium bromide, chloride or methyl sulfate;
 - N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylammonium chloride (DADMAC);
 - polyquaternary monomers such as dimethylaminopropylmethacrylamide chloride and N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT), etc.
 - carboxybetaine monomers

By way of examples of hydrophilic monomers which are potentially cationic in the medium (MAV) mention may be made of

- N,N-(dialkylamino- ω -alkyl)amides of α - β monoethylenically unsaturated carboxylic acids such as N,N-dimethylaminomethylacrylamide or -methacrylamide, 2-(N,N-dimethylamino)ethyl-acrylamide or -methacrylamide, 3-(N,N-dimethylamino)propyl-acrylamide or -methacrylamide, and 4-(N,N-dimethylamino)butyl-acrylamide or -methacrylamide
- α - β monoethylenically unsaturated amino esters such

- as 2-(dimethylamino)ethyl methacrylate (DMAM),
 3-(dimethylamino)propyl methacrylate, 2-(tert-butyl-
 amino)ethyl methacrylate, 2-(dipentylamino)ethyl
 methacrylate, and 2-(diethylamino)ethyl methacrylate
- 5 • monomers which are precursors of amine functions,
 such as N-vinylformamide, N-vinylacetamide, etc.,
 which give rise to primary amine functions by simple
 acid or base hydrolysis.

By way of examples of hydrophilic monomers
 10 which are neutral in the medium (MAV) and potentially
anionic in the rinsing medium (MR) mention may be made
 of

- monomers possessing at least one carboxyl function,
 such as α - β ethylenically unsaturated carboxylic
 15 acids or the corresponding anhydrides, such as
 acrylic, methacrylic, and maleic acid or anhydride,
 fumaric acid, itaconic acid, N-methacryloylalanine,
 N-acryloylglycine and their water-soluble salts
- monomers which are precursors of carboxylate
 20 functions, such as tert-butyl acrylate, which give
 rise, after polymerization, to carboxylic functions
 by hydrolysis.

By way of examples of anionic hydrophilic
monomers (whose first pKa is less than 3) mention may
 25 be made of

- monomers possessing at least one sulfate or sulfonate
 function, such as 2-sulfooxyethyl methacrylate,

vinylbenzene sulfonic acid, allyl sulfonic acid,
2-acrylamido-2-methylpropane sulfonic acid,
sulfoethyl acrylate or methacrylate, sulfopropyl
acrylate or methacrylate and their water-soluble
5 salts

- monomers possessing at least one phosphonate or phosphate function, such as vinylphosphonic acid, etc., the esters of ethylenically unsaturated phosphates, such as the phosphates derived from
10 hydroxyethyl methacrylate (Empicryl 6835 from Rhodia) and those derived from polyoxyalkylene methacrylates, and their water-soluble salts.

By way of examples of hydrophilic monomers which are uncharged or unionizable mention may be made
15 of

- hydroxyalkyl esters of α - β ethylenically unsaturated acids, such as hydroxyethyl and hydroxypropyl acrylate and methacrylate, glyceryl monomethacrylate, etc.
- 20 • α - β ethylenically unsaturated amides such as acrylamide, N,N-dimethylmethacrylamide, N-methylolacrylamide, etc.
- α - β ethylenically unsaturated monomers bearing a water-soluble polyoxyalkylene segment of the
25 polyethylene oxide type, such as polyethylene oxide α -methacrylates (Bisomer S20W, S10W, etc., from Laporte) or α , ω -dimethacrylates, Sipomer BEM from

Rhodia (ω -behenyl polyoxyethylene methacrylate), and Sipomer SEM-25 from Rhodia (ω -tristyrylphenyl polyoxyethylene methacrylate), etc.

- α - β ethylenically unsaturated monomers which are precursors of hydrophilic units or blocks, such as vinyl acetate, which, once polymerized, can be hydrolyzed in order to give rise to vinyl alcohol units or polyvinyl alcohol blocks
- α - β ethylenically unsaturated monomers of ureido type, and in particular 2-imidazolidinone-ethyl methacrylamido (Sipomer WAM II from Rhodia).
By way of examples of zwitterionic monomers mention may be made of
- sulfobetaine monomers such as sulfopropyldimethylammoniummethyl methacrylate (SPE from Raschig), sulfopropyldimethylammoniumpropyl methacrylamide (SPP from Raschig) and sulfopropyl-2-vinylpyridinium (SPV from Raschig)
- phosphobetaine monomers, such as phosphatoethyltrimethylammoniummethyl methacrylate.

By way of examples of crosslinking monomers, mention may be made of

- divinylbenzene
- ethylene glycol dimethacrylate
- allyl methacrylate
- methylenebis(acrylamide)
- glyoxalbis(acrylamide)

- butadiene
- triallyl isocyanurate.

The average molar mass of said polymer (measured by gel permeation chromatography (GPC) THF and expressed in polystyrene equivalents) may be at least 20 000 g/mol, preferably from 50 000 to 1 000 000 g/mol, more preferably of the order of from 100 000 to 1 000 000 g/mol.

Said polymers constituting the active substance (A) may be obtained conventionally, preferably by free-radical polymerization of the ethylenically unsaturated monomers in an aqueous medium. Polymer or copolymer particle dispersions may be obtained in particular by free-radical polymerization in emulsion in water. The polymer dry extract content may be of the order of from 5 to 60% by weight.

Processes which allow small-diameter nanoparticle dispersions to be obtained are described in Colloid Polym. Sci. 266:462-469 (1988) and in Journal of Colloid and Interface Science, Vol. 89, No. 1, September 1982, pages 185 et seq. One way of preparing dispersions of particles with an average size of less than 100 nm, in particular with an average size ranging from 1 to 60 nm, more particularly from 5 to 40 nm, is described in EP-A-644 205.

Preferentially, the choice and relative

amounts of the monomer or monomers from which the polymer constituting the active substance (A) are derived are such that said polymer has a glass transition temperature T_g of the order of from -80°C to $+150^{\circ}\text{C}$, more particularly of the order of from -80°C to $+40^{\circ}\text{C}$.

One first embodiment of the invention consists in employing as active substance (A) an organic polymer which is insoluble in the medium (MAV) and in the rinsing medium (MR).

According to the invention said polymer constituting the active substance (A) is considered to be insoluble when less than 15%, preferably less than 10%, of its weight is soluble in the medium (MAV) and the rinsing medium (MR). The proportion of units derived from potentially anionic monomer which may possibly be present is a function of the nature of the other monomers employed to prepare the active substance; this proportion is generally less than 10% of the total mass of monomers.

Preferentially, said polymer constituting the insoluble active substance (A) is a polymer derived from at least one nonionic hydrophobic monomer, or a copolymer derived from at least one nonionic hydrophobic monomer and from 0.1 to 20% of its weight of at least one monomer which is potentially cationic in the medium (MAV).

A second embodiment of the invention consists in employing as active substance (A) an organic copolymer which is insoluble in the medium (MAV) with a pH of the order of 2 to 5, is capable of swelling in the rinsing medium (MR) with a pH of the order of 5.5 to 8, and is capable of dissolving in the washing bath during a subsequent washing operation at a pH of the order of 8.5 to 11.

Preferentially, said copolymer capable of swelling is derived from at least one nonionic hydrophobic monomer and from 10 to 50% of its weight of at least one monomer which is potentially anionic in the rinsing medium (MR).

Possible examples of polymers constituting the active substance (A) include the following:

- polybutyl acrylates having a Tg of the order of -55°C and an average particle size of the order of 50 nm
- poly-tert-butyl acrylates having an average particle size of the order of 45 nm
- butyl acrylate/diethylaminoethyl methacrylate copolymers, of weight ratio 98/2, having a Tg of the order of -50°C and an average particle size of the order of 60 nm
- butyl acrylate/glyceryl monomethacrylate copolymers, of weight ratio 95/5, having a Tg of the order of -50°C and an average particle size of the order of 50 nm

- butyl acrylate/MAPTAC copolymers, of weight ratio 95/5, having a Tg of the order of -40°C and an average particle size of the order of 50 nm
- butyl acrylate/trimethylammoniummethyl methacrylate chloride copolymers, of weight ratio 95/5, having a Tg of the order of -40°C and an average particle size of the order of 50 nm.

They can be obtained by emulsion polymerization in the presence of 10% by weight of a cationic surfactant such as Dehyquart® ACA from Cognis.

According to the invention the active substance (A) is dispersed stably in the medium (MAV) by means of a surfactant (TAC).

Said surfactant (TAC) present for stabilizing (A) in the formulation may be employed at least in part during the synthesis of the polymer which constitutes the active substance (A).

Said surfactant (TAC) may be a nonionic surfactant and/or a cationic surfactant when the polymer constituting the active substance (A) is intrinsically cationic or intrinsically potentially cationic in the medium (MAV).

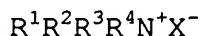
Said surfactant (TAC) is a cationic surfactant or a mixture of cationic surfactant and nonionic surfactant when said polymer constituting the active substance (A) is uncharged or has a zero charge; the amount of nonionic surfactant represents less than 70% of the

weight of all of the surfactants (TAC).

For effective realization of the invention the ratio of the mass of polymer constituting the active substance (A) to the mass of surfactant (TAC) is from 0.01 to 10, preferably from 0.01 to 1.

The cationic charges generated by the optional cationic or potentially cationic units of the polymer constituting the active substance (A) and by the cationic surfactant or surfactants at the surface of the polymer constituting the active substance (A) in dispersion in the medium (MAV) are such that the zeta potential of said polymer or copolymer in dispersion in (MAV) is from 0 to +50 mV, preferably from +10 to +40 mV.

Among cationic surfactants mention may be made in particular of the quaternary ammonium salts of formula



where

- R^1 , R^2 and R^3 , alike or different, represent H or an alkyl group containing less than 4 carbon atoms, preferably 1 or 2 carbon atom(s), which is optionally substituted by one or more hydroxyl function(s), or may form, together with the nitrogen atom N^+ , at least one aromatic or heterocyclic ring,
- R^4 represents a C_8 - C_{22} , preferably C_{12} - C_{22} , alkyl or alkenyl group, an aryl group or benzyl, and

- X^- is a solubilizing anion such as halide (for example, chloride, bromide or iodide), sulfate or alkyl sulfate (methyl sulfate), carboxylate (acetate, propionate or benzoate) or alkyl- or arylsulfonate.
- 5 Mention may be made in particular of dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and cetyltrimethylammonium bromide, stearylpyridinium chloride, Rhodquat® TFR and Rhodamine® C15, sold by Rhodia, cetyltrimethylammonium chloride (Dehyquart ACA
- 10 and/or AOR from Cognis), and cocobis(2-hydroxyethyl)-ethylammonium chloride (Ethoquad C12 from Akso Nobel).

Mention may also be made of other cationic surfactants having softening properties, such as:

- the quaternary ammonium salts of formula
- 15 $R^1'R^2'R^3'R^4'N^+X^-$
- where
- R^1' and R^2' , alike or different, represent H or an alkyl group containing less than 4 carbon atoms, preferably 1 or 2 carbon atom(s), which is optionally
- 20 substituted by one or more hydroxyl function(s), or may form, together with the nitrogen atom N^+ , a heterocyclic ring,
- R^3' and R^4' represent a C_8 - C_{22} , preferably C_{10} - C_{22} , alkyl or alkenyl group, an aryl group or benzyl, and
- 25 • X^- is an anion such as halide (for example, chloride, bromide or iodide), sulfate or alkyl sulfate (methyl sulfate), carboxylate (acetate, propionate or

benzoate) or alkyl- or arylsulfonate.

The following may be mentioned in particular:
dialkyldimethylammonium chlorides such as ditallow
dimethylammonium chloride or methyl sulfate, etc., and
5 alkylbenzyldimethylammonium chlorides.

- C₁₀-C₂₅alkylimidazolium salts such as C₁₀-C₂₅alkyl-
imidazolinium methyl sulfates
- substituted polyamine salts such as N-tallow-
N,N',N'-triethanol-1,3-propylenediamine dichloride
10 or dimethyl sulfate and N-tallow-N,N,N',N',N'-
pentamethyl-1,3-propylenediamine dichloride

Among nonionic surfactants mention may be
made of polyoxyalkenylated derivatives such as

- ethoxylated or ethoxy-propoxylated fatty alcohols
- 15 - ethoxylated or ethoxy-propoxylated triglycerides
- ethoxylated or ethoxy-propoxylated fatty acids
- ethoxylated or ethoxy-propoxylated sorbitan esters
- ethoxylated or ethoxy-propoxylated fatty amines
- ethoxylated or ethoxy-propoxylated di(1-phenyl-
20 ethyl)phenols
- ethoxylated or ethoxy-propoxylated tri(1-phenyl-
ethyl)phenols
- ethoxylated or ethoxy-propoxylated alkyl phenols

The dispersion medium (MAV) for the active
25 substance (A) is an aqueous or aqueous-alcoholic polar
medium.

Alcohols which may be present include ethanol,

isopropanol, propylene glycol, butoxy ethanol, etc.

These alcohols may represent up to 70% of the volume of medium (MAV)

Preferentially the medium (MAV) is water.

- 5 The medium may be brought to the desired pH of from 2 to 5 by addition of an acid, such as hydrochloric acid, citric acid, phosphoric acid, benzoic acid, etc.

The rinsing formulation (F) forming the subject of the invention comprises a vehicle (V) which
10 is capable of bringing the active substance (A) onto the surface of the textile fiber articles in the rinsing operation.

According to the invention said vehicle (V)

- 15 • comprises an organic polymer which is soluble or dispersible in the medium (MAV) and in the rinsing medium (MR)
- has an overall cationic or zero ionic charge in the medium (MAV)
- 20 • is capable, at the pH of the rinsing operation in the rinsing medium (MR), of developing anionic charges in sufficient quantity to destabilize the active substance
25 (A) in the rinsing medium (MR).

Said organic polymer constituting the vehicle (V) may be any polymer which is soluble or dispersible

in aqueous or aqueous-alcoholic medium with a pH of between 2 and 8 and which comprises at least one unit which is neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR).

- 5 They may further comprise at least one unit which is cationic or potentially cationic (HC) in the medium (MAV) and/or at least one hydrophilic or hydrophobic nonionic unit.

The term "dispersible" signifies that the
10 vehicle (V) does not form a macroscopic precipitate in aqueous or aqueous-alcoholic medium.

Preferentially the polymer constituting the vehicle (V) is a copolymer comprising:

- at least one hydrophilic unit which is
15 neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR) and
- at least one hydrophilic unit which is cationic or potentially cationic (HC) in the medium (MAV)
- 20 • and optionally at least one hydrophobic or hydrophilic nonionic unit.

The polymer constituting the vehicle (V) may optionally contain anionic units (whose first pKa is less than 3), but in a very small amount, for example
25 in an amount much less than 5% by weight relative to the entirety of the units.

The relative amounts of the various units of the

polymer constituting the vehicle (V) are such that in the medium (MAV) the overall charge of the polymer or copolymer is zero or cationic.

The relative amounts of vehicle (V) polymer, 5 surfactant (TAC), and polymer constituting the active substance (A) are such that in the course of the rinsing operation the number of anionic charges developed in the rinsing medium (MR) by the vehicle polymer (V) is sufficient to destabilize the active 10 substance (A) in the rinsing medium (MR), in particular by electrostatic attraction with the surface charges of the active substance (A) in the medium (MR).

According to the invention the active substance (A) is considered as being destabilized in 15 the rinsing medium (MR) comprising the vehicle (V) when the turbidity of said medium reaches in less than 5 minutes a value at least 5 times greater than the turbidity that the same medium would have in the absence of vehicle (V).

20 The number of anionic charges developed in the rinsing medium (MR) by the vehicle (V) polymer to destabilize the active substance is preferably at least 1% relative to the number of cationic surface charges of the active substance (A) in the medium (MR).

25 This number of anionic charges may range up to 200% relative to the number of cationic surface charges of the active substance (A) in the medium (MR).

Possible examples that may be mentioned of polymers which may constitute the vehicle (V) include in particular the polymers derived from ethylenically unsaturated monomers, and also natural polysaccharides and substituted or modified polysaccharides, and also mixtures of said polymers derived from ethylenically unsaturated monomers and said polysaccharides.

A first example of polymers which may constitute the vehicle (V) are the polymers derived:

- 10 • from at least one α - β monoethylenically unsaturated monomer which is neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR) and
- optionally at least one α - β monoethylenically unsaturated monomer which is cationic or potentially cationic (HC) in the medium (MAV), and
- 15 • optionally at least one nonionic α - β monoethylenically unsaturated monomer which is hydrophilic or hydrophobic, preferably hydrophilic.

20 Preferentially the (V) is a random, block or graft copolymer derived

- from at least one α - β monoethylenically unsaturated hydrophilic monomer which is neutral in the medium (MAV) and potentially anionic (HA) in the
- 25 rinsing medium (MR) and
- from at least one α - β monoethylenically unsaturated hydrophilic monomer which is cationic or

potentially cationic (HC) in the medium (MAV),

- and optionally from at least one nonionic α - β monoethylenically unsaturated monomer which is hydrophilic or hydrophobic, preferably hydrophilic.

5 The relative amounts of monomers from which (V) is derived are such that in the medium (MAV) the overall charge of the copolymer (V) is zero or cationic.

 The average molar mass of said polymer or
10 copolymer (V) derived from one or more α - β mono-ethylenically unsaturated monomers (measured by aqueous gel permeation chromatography (GPC) and expressed in polyoxyethylene equivalents) is greater than 5 000 g/mol, generally of the order of from 20 000 to
15 500 000 g/mol.

 As examples of hydrophilic α - β mono-ethylenically unsaturated monomer which is neutral in the medium (MAV) and potentially anionic (HA) in the rinsing medium (MR) mention may be made of

- 20 • monomers possessing at least one carboxyl function, such as α - β ethylenically unsaturated carboxylic acids or the corresponding anhydrides, such as acrylic, methacrylic, and maleic acid or anhydride, fumaric acid, itaconic acid, N-methacryloylalanine,
25 N-acryloylglycine and their water-soluble salts
- monomers which are precursors of carboxylate functions, such as tert-butyl acrylate, which give

rise, after polymerization, to carboxylic functions by hydrolysis.

As examples of hydrophilic α - β mono-ethylenically unsaturated monomer which is cationic or
 5 potentially cationic (HC) in the medium (MAV) mention may be made of

- acryloyl- or acryloyloxyammonium monomers such as trimethylammoniumpropyl methacrylate chloride, trimethylammoniummethacrylamide or -methacrylamide
 10 chloride or bromide, trimethylammoniumbutylacrylamide or -methacrylamide methyl sulfate, trimethylammoniumpropylmethacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethyl-
 15 ammonium chloride (APTAC), methacryloyloxyethyltrimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride;
- 1-ethyl-2-vinylpyridinium or 1-ethyl-4-vinylpyridinium bromide, chloride or methyl sulfate;
- 20 • N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylammonium chloride (DADMAC);
- polyquaternary monomers such as dimethylaminopropylmethacrylamide chloride and N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT), etc.
- 25 • carboxybetaine monomers
- N,N-(dialkylamino- ω -alkyl)amides of α - β mono-ethylenically unsaturated carboxylic acids such as

N,N-dimethylaminomethylacrylamide or -methacrylamide,
 2-(N,N-dimethylamino)ethyl-acrylamide or
 -methacrylamide, 3-(N,N-dimethyl-amino)propyl-
 acrylamide or -methacrylamide, and 4-(N,N-
 5 dimethylamino)butyl-acrylamide or -methacrylamide

- α - β monoethylenically unsaturated amino esters such
 as 2-(dimethylamino)ethyl methacrylate (DMAM),
 3-(dimethylamino)propyl methacrylate, 2-(tert-butyl-
 amino)ethyl methacrylate, 2-(dipentylamino)ethyl
 10 methacrylate, and 2-(diethylamino)ethyl methacrylate
- monomers which are precursors of amine functions,
 such as N-vinylformamide, N-vinylacetamide, etc.,
 which give rise to primary amine functions by simple
 acid or base hydrolysis.

15 As examples of hydrophilic α - β mono-
ethylenically unsaturated monomers which are uncharged
or unionizable mention may be made of

- hydroxyalkyl esters of α - β ethylenically unsaturated
 acids, such as hydroxyethyl and hydroxypropyl
 20 acrylate and methacrylate, glyceryl monomethacrylate,
 etc.
- α - β ethylenically unsaturated amides such as
 acrylamide, N,N-dimethylmethacrylamide,
 N-methylolacrylamide, etc.
- 25 • α - β ethylenically unsaturated monomers bearing a
 water-soluble polyoxyalkylene segment of the
 polyethylene oxide type, such as polyethylene oxide

α -methacrylates (Bisomer S20W, S10W, etc., from Laporte) or α,ω -dimethacrylates, Sipomer BEM from Rhodia (ω -behenyl polyoxyethylene methacrylate), and Sipomer SEM-25 from Rhodia (ω -tristyrylphenyl polyoxyethylene methacrylate), etc.

- α - β ethylenically unsaturated monomers which are precursors of hydrophilic units or blocks, such as vinyl acetate, which, once polymerized, can be hydrolyzed in order to give rise to vinyl alcohol units or polyvinyl alcohol blocks
- α - β ethylenically unsaturated monomers of ureido type, and in particular 2-imidazolidinone-ethyl methacrylamide (Sipomer WAM II from Rhodia).

By way of examples of hydrophobic nonionic α - β monoethylenically unsaturated monomers mention may be made of

- vinylaromatic monomers such as styrene, vinyltoluene, etc.
- alkyl esters of α - β monoethylenically unsaturated acids, such as methyl and ethyl acrylate and methacrylate, etc.
- vinyl or allyl esters of saturated carboxylic acids, such as vinyl or allyl acetates, propionates, and versatates
- α - β monoethylenically unsaturated nitriles such as acrylonitrile, etc.

As examples of hydrophilic anionic α - β

monoethylenically unsaturated monomer (whose first pKa is less than 3) mention may be made of

- monomers possessing at least one sulfate or sulfonate function, such as 2-sulfooxyethyl methacrylate,
 5 vinylbenzene sulfonic acid, allyl sulfonic acid,
 2-acrylamido-2-methylpropane sulfonic acid,
 sulfoethyl acrylate or methacrylate, sulfopropyl
 acrylate or methacrylate and their water-soluble
 salts
- 10 • monomers possessing at least one phosphonate or
 phosphate function, such as vinylphosphonic acid,
 etc., the esters of ethylenically unsaturated
 phosphates, such as the phosphates derived from
 hydroxyethyl methacrylate (Empicryl 6835 from Rhodia)
 15 and those derived from polyoxyalkylene methacrylates,
 and their water-soluble salts.

By way of examples of polymers derived from ethylenically unsaturated monomers constituting the vehicle (V) mention may be made of

- 20 • polyacrylic or polymethacrylic acids, alkali metal
 polyacrylates or polymethacrylates, preferably with a
 molar mass by weight of from 100 000 to
 1 000 000 g/mol
- acrylic acid/DADMAC copolymers, with a molar ratio of
 25 50/50 to 30/70, preferably with a molar mass by
 weight of from 70 000 to 350 000 g/mol
- acrylic acid/MAPTAC copolymers, with a molar ratio of

60/40 to 30/70, preferably with a molar mass by weight of from 90 000 to 300 000 g/mol

- acrylic acid/MAPTAC/linear C₄-C₁₈ alkyl methacrylate terpolymers comprising 0.005 to 10% by mass of alkyl methacrylate, with an acrylic acid/MAPTAC molar ratio ranging from 60/40 to 30/70, and preferably having a molar mass by weight of from 50 000 to 250 000 g/mol
- acrylic acid/dimethylaminoethyl methacrylate (DMAEMA) copolymers, with a molar ratio of 60/40 to 30/70, preferably with a molar mass by weight of from 50 000 to 300 000 g/mol.

A second example of polymers which can constitute the vehicle (V) are potentially anionic natural polysaccharides and potentially anionic or amphoteric substituted or modified polysaccharides.

The potentially anionic natural polysaccharides are formed of nonionic monosaccharide units and of monosaccharide units which are neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR), these units being alike or different. They may be linear or branched.

More particularly said potentially anionic natural polysaccharides are branched polysaccharides formed

- of a main chain comprising alike or different anhydrohexose units
- and of branches comprising at least one

anhydropentose and/or anhydrohexose unit which is neutral in the medium (MAV) and optionally potentially anionic in the rinsing medium (MR).

5 The hexose units (alike or different) of the main chain may be units of D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, etc.

 The pentose and/or hexose units (alike or different) which are nonionic or neutral in the medium
10 (MAV) and potentially anionic in the medium (MR) of the branches may be units of D-xylose etc., L- or D-arabinose, D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, D-glucuronic acid, D-galacturonic acid, D-mannuronic acid, D-mannose
15 substituted by a pyruvic group, etc.

 By way of examples of natural polysaccharides which are neutral in the medium (MAV) and potentially anionic in the rinsing medium (MR) mention may be made of xanthan gum (such as the Rhodopol® products from
20 Rhodia), succinoglycans, rhamsans, gellan gums, welan gums, etc.

 Their molar mass by weight may range from 2 000 to 5 000 000, preferably from 10 000 to 5 000 000, more particularly from 10 000 to
25 4 000 000 g/mol.

 The molar mass by weight M_w of said polysaccharides may be measured by size exclusion chromatography.

When the polysaccharides in question are substituted or modified, their native skeleton is formed of nonionic monosaccharide units and/or of monosaccharide units which are neutral in the medium
5 (MAV) and potentially anionic in the rinsing medium (MR), said monosaccharide units being alike or different and being substituted or modified

- by one or more groups which carry at least one charge which is neutral in the medium
10 (MAV) and potentially anionic in the medium (MR)
- and optionally by one or more groups which carry at least one charge which is cationic or potentially cationic in the medium (MAV),
15 the degree of substitution or modification of the monosaccharide units by the entirety of the groups which carry charges which are potentially anionic and of optional groups which carry cationic charges being such that said substituted or modified polysaccharide
20 is soluble or dispersible in aqueous or aqueous-alcoholic medium and has an overall cationic or zero charge in the medium (MAV).

Said substituted or modified polysaccharides may further comprise at least one nonionic modifying or
25 substituent group.

Among the native skeletons which can be employed mention may be made of linear or branched

polysaccharides.

More particularly said polysaccharide is a substituted or modified branched polysaccharide whose native skeleton is formed

- 5 • of a main chain comprising alike or different anhydrohexose units
- and of branches comprising at least one anhydropentose and/or anhydrohexose unit which is neutral in the medium (MAV) and
- 10 optionally potentially anionic in the rinsing medium (MR),

the anhydrohexose and/or anhydropentose units of said polysaccharide being substituted or modified by one or more groups which carry at least one charge which is

15 neutral in the medium (MAV) and potentially anionic in the medium (MR) and optionally at least one charge which is cationic or potentially cationic in the medium (MAV),

the degree of substitution or modification D_{Si} of the

20 anhydrohexose and/or anhydropentose units by the entirety of said groups which carry charges which are ionic or potentially ionic ranging from 0.01 to less than 3, preferably from 0.01 to 2.5,

with a ratio of the number of potentially anionic

25 charges in the medium (MR) to the number of cationic or potentially cationic charges in the medium (MAV) ranging from 100/0 to 30/70, preferably from 100/0 to

50/50.

When the polysaccharide in question is amphoteric the ratio of the number of charges which are potentially anionic in the medium (MR) to the number of
5 charges which are cationic or potentially cationic in the medium (MAV) is from 99.5/0.5 to 30/70, preferably from 99.5/0.5 to 50/50.

Said substituted or modified branched polysaccharide may further comprise at least one
10 nonionic modifying or substituent group.

The molar mass by weight of said substituted or modified polysaccharides may range from 2 000 to 5 000 000, preferably from 10 000 to 5 000 000 g/mol. The molar mass by weight, M_w , of said polysaccharides
15 may be measured by size exclusion chromatography.

When the polysaccharide in question carries substituent groups which are potentially anionic in the medium (MR) the measurement is made in water at a pH of 9-10 containing 0.1 M LiCl and 2/10 000 of sodium
20 nitrate.

When the polysaccharide in question is amphoteric, i.e., carries substituent groups which are potentially anionic in the medium (MR) and groups which are cationic or potentially cationic in the medium
25 (MAV), the measurement is made in a 0.1 M aqueous formic acid solution containing 0.05 M sodium nitrate and 10 ppm of high molar mass polyallyldimethylamine

chloride (PDADMA) in the case of polysaccharides whose DSi in terms of ionic or potentially ionic function is less than 0.5. For those whose DSi is greater than 0.5 a 0.025 M aqueous hydrochloric acid solution is used.

- 5 The molar mass by weight, M_w , is established directly in a known manner by means of the light scattering values.

The degree of substitution or of modification, DSi, corresponds to the average number of
10 hydroxyl functions of the anhydrohexose and/or anhydropentose units which are substituted or modified by said ionic or potentially ionic group or groups per anhydrohexose and/or anhydropentose unit.

Said ionic or potentially ionic groups are
15 linked to the carbon atoms of the sugar skeleton either directly or by way of -O- bonds.

In the case of amphoteric polysaccharides the potentially anionic charges may be provided by modifying groups or substituent groups which are
20 different from those which carry cationic or potentially cationic charges; in that case said polymer is an ampholyte polysaccharide.

When a modifying group or substituent group at the same time carries a potentially anionic charge
25 and a cationic or potentially cationic charge, said polysaccharide is in that case of betaine type.

Said substituted or modified polysaccharide

may further exhibit at least one nonionic modifying group or substituent group. Said nonionic groups are attached to the carbon atoms of the sugar skeleton either directly or by way of -O- bonds. The presence of

5 such groups is expressed in number of moles of substitution MS, i.e., in average number of moles of precursor of said nonionic substituent which have reacted per anhydrohexose and/or anhydropentose unit. If said precursor is not appropriate for forming new,

10 reactive hydroxyl groups (alkylation precursor, for example), the degree of substitution or of modification by the entirety of the ionic or ionizable groups and nonionic groups is less than 3 by definition.

If said precursor is capable of forming new, reactive

15 hydroxyl groups (hydroxyl alkylation precursor, for example), there is theoretically no limit on the number of moles of substitution, MS; it may, for example, be up to 6, preferably up to 2.

Among the groups which are potentially

20 anionic in the medium (MR) mention may be made of those containing one or more carboxylate (carboxylic) functions.

Mention may be made in particular of those of formula

-[-CH₂-CH(R)-O]_x-(CH₂)_y-COOH or

25 -[-CH₂-CH(R)-O]_x-(CH₂)_y-COOM

where

R is a hydrogen atom or an alkyl radical containing 1

to 4 carbon atoms

x is an integer ranging from 0 to 5

y is an integer ranging from 0 to 5

M represents an alkaline metal.

5 Very particular mention may be made of the carboxy groups $\text{-COO}^-\text{Na}^+$ attached directly to a carbon atom of the sugar skeleton and of carboxy methyl (sodium salt) groups $\text{-CH}_2\text{-COO}^-\text{Na}^+$ attached to a carbon atom of the sugar skeleton via an -O- bond.

10 Among cationic or potentially cationic groups mention may be made of those which contain one or more amino, ammonium, phosphonium, pyridinium, etc., functions.

 Mention may be made in particular of the
15 cationic or potentially cationic groups of formula

- -NH_2
- $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-(CH}_2)_y\text{-COA-R'-N(R'')}_2$
- $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-(CH}_2)_y\text{-COA-R'-N}^+(\text{R''')}_3 \text{X}^-$
- $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-(CH}_2)_y\text{-COA-R'-NH-R''''-N(R'')}_2$
- 20 • $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-R'-N(R'')}_2$
- $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-R'-N}^+(\text{R''')}_3 \text{X}^-$
- $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-R'-NH-R''''-N(R'')}_2$
- $\text{-}[\text{-CH}_2\text{-CH(R)-O}]_x\text{-Y-R''}$

where

- 25 ▪ R is a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms
- x is an integer ranging from 0 to 5

- y is a integer ranging from 0 to 5
- R' is an alkylene radical containing 1 to 12 carbon atoms, optionally carrying one or more OH substituents
- the radicals R'', which are alike or different,
- 5 represent a hydrogen atom or an alkyl radical containing from 1 to 18 carbon atoms
- the radicals R''', which are alike or different, represent an alkyl radical containing 1 to 18 carbon atoms
- 10 ▪ R'''' is a linear, branched or cyclic alkylene radical containing 1 to 6 carbon atoms
- A represents O or NH
- Y is a heterocyclic aliphatic group containing 5 to 20 carbon atoms and one nitrogen heteroatom
- 15 ▪ X⁻ is a counterion, preferably halide (chloride, bromide and iodide in particular), and N-alkylpyridinium-yl groups whose alkyl radical contains 1 to 18 carbon atoms, with a counterion, preferably halide (chloride, bromide and iodide in
- 20 particular).

Among cationic or potentially cationic groups mention may be made very particularly of:

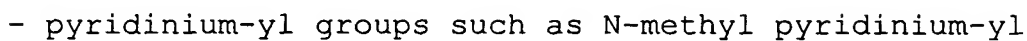
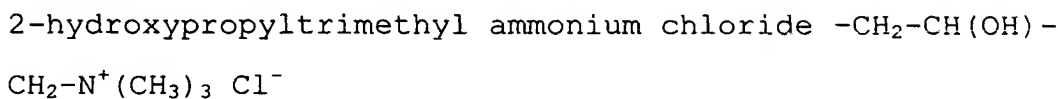
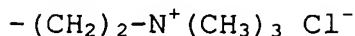
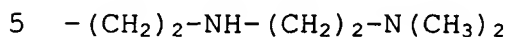
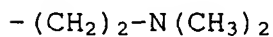
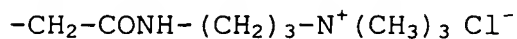
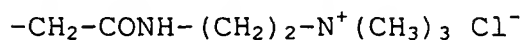
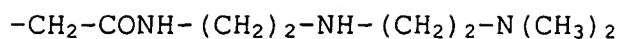
- those of formula

-NH₂

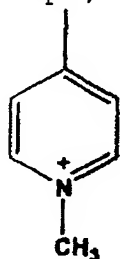
25 -CH₂-CONH-(CH₂)₂-N(CH₃)₂

-CH₂-COO-(CH₂)₂-NH-(CH₂)₂-N(CH₃)₂

-CH₂-CONH-(CH₂)₃-NH-(CH₂)₂-N(CH₃)₂

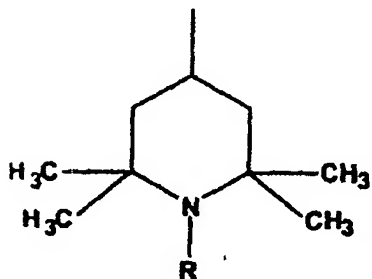


10 groups, of formula



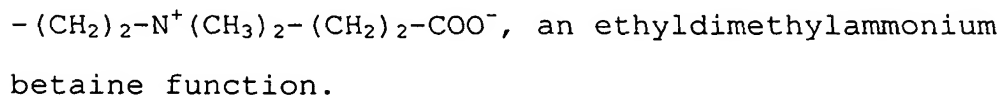
with a chloride counterion

- hindered amino groups such as those derived from HALS amines of general formula



15 where R represents CH₃ or H.

Among betaine groups mention may be made more particularly of the function of formula



20

Among nonionic groups mention may be made of

those of formula

▪ $[-CH_2-CH(R)-O]_x-R^1$ where

R is a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms

5 x is an integer ranging from 0 to 5

R^1 represents

- a hydrogen atom
- an alkyl radical containing 1 to 22 carbon atoms which is optionally interrupted by one or more
- 10 oxygen and/or nitrogen heteroatoms, cycloalkyl, aryl or arylalkyl, containing 6 to 12 carbon atoms

- a radical $-(CH_2)_y-COOR^2$
- a radical $-(CH_2)_y-CN$
- a radical $-(CH_2)_y-CONHR^2$

15 where R^2 represents an alkyl, aryl or arylalkyl radical containing 1 to 22 carbon atoms, and y is an integer ranging from 0 to 5

- $-CO-NH-R^1$,

where R^1 is as defined above,

20 attached to a carbon atom of the sugar skeleton via an -O- bond.

Very particular mention may be made of the following groups:

- methyl, ethyl, propyl, isopropyl, butyl, hexyl,
- 25 octyl, dodecyl, octadecyl, phenyl and benzyl, which are attached to a carbon atom of the sugar skeleton by way of ether, ester, amide or urethane linkage,

- cyanoethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl, which are attached to a carbon atom of the sugar skeleton by way of an -O- bond.

The hexose units (alike or different) of the main chain of the native skeleton may be units of D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, etc.

The pentose and/or hexose units (alike or different) which are nonionic or neutral in the medium (MAV) and potentially anionic in the medium (MR) of the branches of the native skeleton may be units of D-xylose, etc., L- or D-arabinose, D-glucose, D- or L-galactose, D-mannose, D- or L-fucose, L-rhamnose, D-glucuronic acid, D-galacturonic acid, and D-mannuronic acid.

Examples of native skeletons that may be mentioned include galactomannans, galactoglucomannans, xyloglucans, xanthan gums, scleroglucans, succinoglycans, rhamsans, welan gums, etc.

Preferentially the native skeleton is a galactomannan.

The galactomannans are macromolecules containing a main chain of D-mannopyranose units attached in $\beta(1-4)$ position which is substituted by D-galactopyranose units in $\alpha(1-6)$ position. Among these mention may be made of guar gum, carob gum, and tara gum.

Very preferentially the native skeleton is a guar gum.

Guar gums have a mannose/galactose ratio of 2.

The substituted or modified polysaccharides used according to the invention may be obtained by functionalizing the native skeleton by means of
5 precursors of the ionic or potentially ionic groups and optionally nonionic groups.

These operations of functionalization may be carried out in a known way by oxidation, substitution, condensation, and/or addition.

- 10 Examples of substituted or modified polysaccharides which can be used according to the invention include
- carboxymethylgalactomannans, especially carboxymethylguars,
 - 15 - carboxymethylhydroxypropylgalactomannans, especially carboxymethylhydroxypropylguars,
 - carboxymethyl-hydroxypropyltrimethylammonium chloride galactomannans, especially carboxymethyl-
 - 20 hydroxypropyltrimethylammonium chloride guars,
 - carboxymethylhydroxypropyl-hydroxypropyl-trimethylammonium chloride galactomannans, especially carboxymethyl-hydroxypropyl-
 - 25 hydroxypropyltrimethylammonium chloride guars.

When the vehicle (V) is a polysaccharide it

is preferable for the dispersion of the active substance (A) in the medium (MAV) comprising the vehicle (V) to have a pH ranging from 3.5 and in particular from 4.5 to 5 when said polysaccharide is a substituted or modified guar.

For effective realization of the invention the amount of vehicle (V) present in the formulation according to the invention is from 0.001 to 5 parts by weight, preferably from 0.01 to 4 parts, and more particularly from 0.05 to 2 parts by weight per 100 parts by weight of active substance (A).

The formulation (F) according to the invention may be in the form

- of a stable dispersion (liquid, cream, paste, gel, etc)
- or in solid form (powder, granules, block, tablet, etc).

The formula (F) in the form of a stable dispersion may be obtained by

- 1) preparing an aqueous dispersion of polymer constituting the active substance (A) by polymerization in aqueous emulsion in the presence of a surfactant (TAC) as stabilizer; the dry extract of the resulting dispersion may be of the order of from 5 to 60% by weight;
- 2) optionally diluting with water or a water/alcohol mixture (depending on the desired proportion of

active substance A in the formulation F) and adjusting the pH to a value of 2.5 - 5 using an acid (hydrochloric acid, citric acid, phosphoric acid, benzoic acid, etc);

- 5 • 3) adding the vehicle (V) to the resulting dispersion;
- 4) optionally adding an additional amount of surfactant (TAC) before or after adding said vehicle, and
- 10 • 5) if necessary readjusting the pH to a value of from 2.5 - 5 using an acid.

For effective realization of the invention the aqueous or aqueous-alcoholic formulation (F) comprises per 100 parts of its weight

- 15 - from 0.01 to 40, preferably from 0.05 to 30 parts by dry weight of active substance (A)
- from 0.01 to 50, preferably from 0.01 to 35 parts by dry weight of surfactant (TAC)
- from 0.001 to 4, preferably from 0.01 to 1 part by
- 20 dry weight of vehicle (V) polymer.

Said dispersion may have a solids content of from 0.021 to 90%, preferably from 0.07 to 51% by weight.

The formulation (F) in the form of a solid may be obtained by

- 25 • 1) preparing an aqueous dispersion of polymer constituting the active substance (A) by polymerization in aqueous emulsion in the presence of

a surfactant (TAC) as stabilizer; the dry extract of the resulting dispersion may be of the order of from 5 to 60% by weight;

- 2) adjusting the pH to a value of 2.5 - 5 using an acid (hydrochloric acid, citric acid, phosphoric acid, benzoic acid, etc);
- 3) adding the vehicle (V) to the resulting dispersion;
- 4) optionally adding an additional amount of surfactant (TAC) before or after adding said vehicle, and
- 5) if necessary readjusting the pH to a value of from 2.5 - 5 using an acid;
- evaporating/drying.

The evaporating/drying step may be carried out in accordance with any means known to the skilled worker, in particular by lyophilization (i.e., freezing, then sublimation) or, preferably, by spray drying.

Spray drying may be carried out in any known apparatus, such as a spraying tower in combination with a spraying operation carried out by a nozzle or a turbine with a stream of hot air. The implementation conditions are dependant on the type of atomizer used; these conditions are generally such that the temperature of the entirety of the product in the course of drying is at least 30°C and does not exceed 150°C.

The evaporating/drying step may be facilitated by the

presence within the dispersion which is subjected to said step of a protectant, in particular by the presence of at least one sugar, saccharide or polysaccharide which is water-soluble or water-dispersible, preferably a sugar. The amount of protectant may represent of the order of from 10 to 50 parts by weight per 100 parts by weight of active substance (A).

Among sugars mention may be made of aldoses such as glucose, mannose, galactose, and ribose and of ketoses such as fructose.

The granules obtained may be ground to give a powder or compacted conventionally to give tablets, for example.

The formulation (F) may further comprise other, customary constituents of cationic rinsing formulations.

It may in particular comprise at least one cationic and/or nonionic softener, such as acyclic quaternary ammonium compounds, alkoxylated polyamines, quaternary diamido ammonium salts, quaternary ammonium esters, quaternary imidazolium salts, primary, secondary or tertiary amines, alkoxylated amines, cyclic amines, nonionic sugar derivatives, etc., which are mentioned in particular in WO 00/68352. Examples of some of these cationic softeners have already been mentioned earlier on as surfactant (TAC).

The softeners may be present in a proportion

of from 0.5 to 90%, preferably from 0.5 to 40%,
depending on the concentration of said formulation (F).

Also present may be:

- optical brighteners (0.1 to 0.2%)
- 5 - color transfer inhibitors (polyvinylpyrrolidone,
polyvinylloxazolidone, polymethacrylamide, etc. 0.03
to 25%, preferably 0.1 to 15%)
- water-soluble monovalent mineral salts, such as
sodium, potassium or ammonium chlorides, nitrates or
10 sulfates (especially when the vehicle (V) is a
polysaccharide), in a proportion, for example, of
from 0.01 to 2 mol per liter
- silicone oils,
- animal, vegetable or mineral hydrocarbon waxes or
15 oils,
- dyes,
- fragrances,
- foam suppressants
- enzymes
- 20 - bleaches.

The formulation (F) of the invention may be
employed to carry out a rinsing operation which follows
an operation of washing - by hand or in a washing
machine - textile fiber articles. Said articles may
25 consist of natural and/or artificial and/or synthetic
fibers.

Said formulation is especially advantageous

for rinsing cotton or cotton-based articles.
It may be employed in the rinsing bath in a proportion
of from 0.001 to 5 g/l, preferably from 0.005 to 2 g/l,
the proportion of formulation being expressed in terms
5 of dry matter. This rinsing operation may be carried
out at ambient temperature.

This rinsing operation makes it possible to
impart to said articles, in addition to the
conventional benefits of softness which are provided by
10 the nonionic and/or cationic softener or softeners,
properties of wrinkle resistance (antiwrinkle
properties) and/or of ease of ironing, of abrasion
resistance, and soil release properties, which are
provided by the deposition of the active substance (A)
15 on the surface of said articles, this deposition being
promoted by the presence of the vehicle (V).
Advantageous soil release properties are provided in
particular through the use as active substance (A) in
the formulation (F) of a copolymer capable of swelling
20 in the rinsing medium (MR). Such a type of copolymer
has the advantage, following deposition on the textile
surface at the rinsing pH, of being removed on
subsequent washing at basic pH, at the same time as the
soiling.

25 According to one variant embodiment of the
first subject of the invention said solid active
substance (A) in particulate form in the formulation

(F) contains, encapsulated within its particles, at least one liquid or solid hydrophobic organic active substance (MAO) other than (A).

The hydrophobic active substance (MAO) is not miscible
5 with water or is only very slightly miscible with water; this means that its solubility in water at a pH of 7 is less than 20% by weight, preferably less than 10% by weight.

The term active substance (MAO) signifies not only a
10 pure active substance as it is or in a solvent but also a mixture of active substances as they are or in a solvent.

Possible examples of active substance (MAO) include fragrances, biocides (bactericides, fungicides, etc.)
15 which are hydrophobic, anti-UV agents (vanillin, etc.), optical brighteners (stilbene derivatives, etc.), silicone or aminosilicone oils, mineral or vegetable oils, etc.

Said active substance (MAO) may be introduced into the
20 particles of the active substance (A) in a known manner.

It may be introduced in particular during the actual synthesis of the particles of active substance (A), in particular in dissolved form in at least one of the
25 monomers from which the active substance (A) is derived.

If it is liquid and sufficiently "swells" the polymer

or copolymer constituting the active substance (A), the substance (MAO) may also be introduced directly into the dispersion of active substance (A) obtained by emulsion polymerization; if necessary, a "transfer" solvent which swells the polymer or copolymer may be employed. Possible examples of transfer solvents include esters, ketones, alcohols, aliphatic, cycloaliphatic, and aromatic hydrocarbons, which may optionally be chlorinated, and dialkyl ethers. The transfer solvent may subsequently be removed by evaporation.

The amount of hydrophobic organic active substance (MAO) present in the particles of active substance (A) may range from 20 to 70 parts, preferably from 40 to 60 parts by weight per 100 parts by weight of active substance (A).

The presence of the vehicle (V) makes it possible to increase the deposition of the organic active substance (MAO), encapsulated in the active substance (A), on the surface of the textile fiber articles. This is manifested in increased retention of the organic active substance (MAO) on said surface and in better provision to said surface of the intrinsic properties of said substance (MAO). This is especially advantageous when the organic active substance (MAO) is a fragrance.

The invention secondly provides a process for

treating textile fiber articles by contacting said articles in the course of a rinsing operation in aqueous or aqueous-alcoholic medium with the rinsing formulation (F) as described above, then recovering
5 said rinsed articles.

The operating conditions of such a treatment have already been mentioned above.

The invention thirdly provides a process for enhancing the antiwrinkle and/or easy-iron and/or soil
10 release properties of textile fiber articles which consists in contacting said articles in the course of a rinsing operation in aqueous or aqueous-alcoholic medium with the rinsing formulation (F) as described above, then in recovering said rinsed articles.
15 The operating conditions for carrying out such a process have already been mentioned above.

The invention fourthly provides for the use in a formulation (F) intended for use in an operation of rinsing (R) textile fiber articles (S) by means of
20 an aqueous or aqueous-alcoholic medium (MR), formulation (F) comprising at least one active substance (A) comprising at least one solid organic polymer in particulate form and being

- in the form of a stable dispersion with a
25 pH of from 2 to 5 of said active substance (A) in an aqueous or aqueous-alcoholic medium (MAV) or

- in a solid form obtained by drying said dispersion,
- the nature of the active substance (A) and of the aqueous or aqueous-alcoholic medium (MAV) being such
- 5 that the active substance (A)
- is insoluble in the medium (MAV)
 - has an overall zero or cationic charge in the medium (MAV),
 - is stabilized in the medium (MAV) by means
- 10 of a cationic surfactant (TAC), it being possible for said cationic surfactant (TAC) to be wholly or partly replaced by a nonionic surfactant when the polymer constituting the active substance (A) is
- 15 intrinsically cationic or intrinsically potentially cationic in the medium (MAV)
- remains insoluble in the rinsing medium (MR) or is capable of swelling in the rinsing medium (MR);
- 20 of at least one organic polymer which
- ◆ is soluble or dispersible in the medium (MAV) and in the rinsing medium (MR)
 - ◆ has an overall cationic or zero ionic charge in the medium (MAV)
 - 25 ◆ and is capable, at the pH of the rinsing operation in the rinsing medium (MR), of developing anionic charges in sufficient quantity to destabilize the

active substance (A) in the rinsing medium (MR);
as a vehicle (V) capable of bringing said active
substance (A) toward the surface of said textile fiber
articles (S) in the rinsing operation (R).

5 In one variant embodiment of this fourth
subject of the invention the active substance (A)
contains, encapsulated in its particles, at least one
hydrophobic organic active substance (MAO), and said
vehicle or organic polymer (V) is capable of bringing
10 the organic active substance (MAO) encapsulated in the
active substance (A) to the surface of the textile
fiber articles and also of conferring on said surface
the intrinsic properties of said organic active
substance (MAO).

15 The nature and the relative amounts of the
various constituents, their conditions of use, and the
operating conditions to be employed have already been
set out above.

 The invention fifthly provides a process for
20 enhancing the deposition of an active substance (A)
comprising at least one solid organic polymer in
particulate form, optionally containing encapsulated in
its particles a hydrophobic organic substance (MAO), on
the surface of textile fiber articles (S), during an
25 operation of rinsing of said articles by means of an
aqueous or aqueous-alcoholic medium (MR) obtained from
a formulation (F) comprising said active substance (A),

the formulation (F) being

- in the form of a stable dispersion with a pH of from 2 to 5 of said active substance (A) in an aqueous or aqueous-alcoholic medium (MAV) or
- in a solid form obtained by drying said dispersion,

the nature of the active substance (A) and of the aqueous or aqueous-alcoholic medium (MAV) being such that the active substance (A)

- is insoluble in the medium (MAV)
- has an overall zero or cationic charge in the medium (MAV),
- is stabilized in the medium (MAV) by means of a cationic surfactant (TAC), it being possible for said cationic surfactant (TAC) to be wholly or partly replaced by a nonionic surfactant when the polymer constituting the active substance (A) is intrinsically cationic or intrinsically potentially cationic in the medium (MAV)
- remains insoluble in the rinsing medium (MR) or is capable of swelling in the rinsing medium (MR);

by adding to said formulation (F) a vehicle (V)

comprising at least one organic polymer which

- ♦ is soluble or dispersible in the medium (MAV) and in

the rinsing medium (MR)

- ◆ has an overall cationic or zero ionic charge in the medium (MAV)
- ◆ and is capable, at the pH of the rinsing operation in the rinsing medium (MR), of developing anionic charges in sufficient quantity to destabilize the active substance (A) in the rinsing medium (MR).

The nature and the relative amounts of the various constituents, their conditions of use and the operating conditions to be employed have already been set out above.

The examples which follow are given by way of illustration.

Example 1: Antiwrinkle and easy-iron effect

15 **Formulation I1**

Use is made of an aqueous dispersion (latex) of a polybutyl acrylate (active substance A) having a molar mass by weight of 500 000 g/mol, a particle size of 35 nm, obtained by emulsion polymerization of butyl acrylate in the presence of 10 parts by weight of cetyltrimethylammonium bromide (surfactant TAC) per 100 parts by weight of butyl acrylate.

The dispersion has a dry extract of 28% by weight.

The pH of this dispersion is adjusted to 4.0 with 1N hydrochloric acid solution. The dispersion is slightly opalescent.

20 ml of the dispersion is poured with mechanical

stirring into 1 ml of water whose pH has been adjusted to 4. This gives a mixture with a pH = 4 whose appearance is not significantly different from that of the original dispersion. This mixture is stable for several days, does not form a precipitate and does not change in turbidity over time.

Formulation III

Use is made of an aqueous dispersion (latex) of a polybutyl acrylate (active substance A) having a particle size of 35 nm, obtained by emulsion polymerization of butyl acrylate in the presence of 10 parts by weight of cetyltrimethylammonium bromide (surfactant TAC) per 100 parts by weight of butyl acrylate.

15 The dispersion has a dry extract of 28% by weight. The pH of this dispersion is adjusted to 4.0 with 1N hydrochloric acid solution. The dispersion is slightly opalescent.

Also prepared is a 2.2% by weight aqueous solution of a 1:1 molar acrylic acid-DADMAC copolymer (with a molar mass of 100 000 g/mol) (vehicle V), the solution having been adjusted to a pH of 4.0 with 10% by weight hydrochloric acid solution.

20 ml of the dispersion of active substance (A) are poured into 1 ml of the vehicle (V) copolymer solution under mechanical stirring. This gives a mixture with a pH of 4 whose appearance is not significantly different

from that of the original dispersion. This mixture is stable for a number of days, does not form any precipitate and does not change in turbidity over time.

Dilute formulations I1(a) and II1(a) obtained by

5 **diluting formulations I1 and II1 in water at a pH of 4**

Two beakers are prepared, each containing 200 ml of water whose pH has been adjusted to 4 with hydrochloric acid.

Under mechanical stirring, 0.1 ml of formulation I1 is
10 added to one beaker and 0.1 ml of the formula II1 to the other, and the turbidity of the mixture is monitored over time. The change in turbidity remains small and no particles are seen to form over time. The results are given in table 1.

15 The turbidity measurements were carried out using a Metrohm turbidimetry cell coupled to a Metrohm photometer; the turbidity value is obtained by comparing the light transmittance in the cell in air and then in the medium under study.

20 **Table 1:**

Time (min)	Turbidity (arbitrary units) Formulation I1(a)	Turbidity (arbitrary units) Formulation II1(a)
1	0.02	0.03
2	0.023	0.033
3	0.025	0.035
4	0.027	0.037
5	0.029	0.039

7	0.032	0.043
10	0.036	0.047

**Dilute formulations I1(b) and III1(b) obtained by
diluting formulations I1 and III1 in water at a pH of
7.2**

- 5 Two beakers are prepared, each containing 200 ml of water at its natural pH of 7.2.
- Under mechanical stirring, 0.1 ml of formulation I1 is added to one beaker and 0.1 ml of the formula III1 to the other, and the turbidity of the mixture is
- 10 monitored over time. The results are given in table 2.
- The turbidity of the solution containing the acrylic acid/DADMAC copolymer is observed to increase significantly over time.

Table 2:

Time (min)	Turbidity (arbitrary units) Formulation I1(b)	Turbidity (arbitrary units) Formulation III1(b)
1	0.024	0.025
2	0.036	0.067
3	0.049	0.149
4	0.059	0.28
5	0.068	0.472
7	0.087	0.633
10	0.118	0.725

- 15 Effect of the (V)/(A) weight ratio: amount of vehicle
(V)/amount of active substance (A)

Use is made of an aqueous dispersion (latex) of a polybutyl acrylate (active substance A) having a particle size of 35 nm, obtained by emulsion polymerization of butyl acrylate in the presence of 5 10 parts by weight of cetyltrimethylammonium bromide (surfactant TAC) per 100 parts by weight of butyl acrylate.

The dispersion has a dry extract of 28% by weight. The pH of this dispersion is adjusted to 4.0 with 1N 10 hydrochloric acid solution. The dispersion is slightly opalescent.

Also prepared is a 22% by weight aqueous solution of a 1:1 molar acrylic acid-DADMAC copolymer (with a molar mass of 100 000 g/mol) (vehicle V), the pH of the 15 solution having been adjusted to 4.0 with 10% by weight hydrochloric acid solution.

20 ml of the dispersion of active substance (A) are poured respectively into 4 ml (formulation 1), 0.1 ml (formulation 2), 0.05 ml (formulation 3) and 0.025 ml 20 (formulation 4) of the solution of vehicle (V) copolymer under mechanical stirring.

Formulations 2, 3 and 4 are made up respectively with 3.9 ml, 3.95 ml and 3.975 ml of water, so as to keep the active substance (A) concentration constant.

25 This gives four formulations with a pH of 4 whose appearance is not significantly different from that of the original dispersion and in which the (V)/(A) weight

ratios are 14.8/100, 0.37/100, 0.18/100 and 0.09/100 respectively.

Four beakers are prepared each containing 200 ml of water at its natural pH of 7.2.

- 5 0.1 ml of formulation is added to each beaker under mechanical stirring, and the turbidity of the mixture is monitored over time.

The turbidity measurements were carried out using a Metrohm turbidimetry cell coupled to a Metrohm

- 10 photometer; the turbidity value is obtained by comparing the light transmittance in the cell in air and then in the medium under study.

The results of turbidity measurements are given in table 3 below:

15 **Table 3**

Time (min)	Turbidity (arbitrary units)			
	(V) / (A)	(V) / (A)	(V) / (A)	(V) / (A)
	14.8/100	0.37/100	0.18/100	0.09/100
1	0.02	0.03	0.03	0.03
2	0.015	0.07	0.035	0.04
5	0.05	0.48	0.09	0.075
7	0.04	0.64	0.15	0.09
10	0.03	0.72	0.22	0.12

These results show that the (V)/(A) ratio has an effect on the capacity of the vehicle (V) to flocculate the active substance (V)

Deposition of the actives on cotton

- 20 The turbidity of above formulations I1(a), II1(a),

I1(b), and III1(b) is measured 30 minutes after their preparation (this turbidity is called "initial turbidity" in table 4 below).

3 squares of woven cotton each of 6 × 6 cm are then
5 soaked in each of said formulations I1(a), III1(a), I1(b), and III1(b), which are kept under mechanical stirring.

The cotton squares are withdrawn from the beakers after 30 minutes of soaking.

10 The turbidity of the dilute formulations which remain is then measured. The results are given in table 4.

Table 4

	Formul. I1(a) (pH 4)	Formul. III1(a) (pH 4)	Formul. I1(b) (pH 7.2)	Formul. III1(b) (pH 7.2)
"Initial turbidity"	0.047	0.059	0.151	0.96
Turbidity after 30 min of soaking	0.043	0.051	0.124	0.49
Effectiveness of deposition	8.5%	13.5%	17.9%	49%

For a given formulation, the variation in turbidity (between the "initial turbidity" and the turbidity
15 after 30 minutes of soaking and withdrawal of the cotton squares) is directly linked to the variation in the concentration of active substances in said formulation after 30 minutes of soaking and withdrawal of the cotton squares. The variation in turbidity

observed therefore allows the effectiveness of deposition to be evaluated, that is the % of active substances which has been deposited on the cotton squares.

- 5 It is observed that the presence of the acrylic acid/DADMAC copolymer in formulation II1b (formulation III1 diluted to give a final pH of 7.2) allows a considerable increase (more than 200%) in the effectiveness of deposition on the cotton of particles
10 present in the dispersion.

Washing machine test

The following three rinsing formulations are prepared or employed:

- * 50 ml of a commercial softener formulation
 - 15 FR, containing only cationic surfactants (15% solids)
 - * a softener formulation FRI1(a) consisting of 10 ml of the diluted formulation FI1(a) above, of pH = 4, corresponding to 186 mg of active substance (A) per liter of formulation FRI1(a)
 - 20 * a softener formulation FRII1 (a) consisting of 10 ml of the diluted formulation FII1(a) above, of pH = 4, corresponding to 186 mg of active substance (A) per liter of formulation FRII1(a)
- 1.5 kg of flat cotton fabric samples measuring
25 50 cm × 50 cm (their finish having been removed beforehand by three successive washes with demineralized water at 90°C) are washed at 30°C using a

commercial powder detergent formulation in a Miele® washing machine (from Miele).

At the end of the wash cycle one of the samples is placed in reserve and rinsed with 15 liters of mains
5 water at 23°C, then wrung; the rinse cycle lasts 5 minutes. The other samples are divided into three batches.

The first batch is rinsed for 5 minutes with 15 liters of the mains water at 23°C, to which 50 ml of
10 formulation FR have been added, then is wrung under the same conditions as the reserved sample.

The second batch is rinsed for 5 minutes with 15 liters of the mains water at 23°C, to which 10 ml of
formulation FRI1(a) have been added, then is wrung
15 under the same conditions as the reserved sample.

The third batch is rinsed for 5 minutes with 15 liters of the mains water at 23°C, to which 10 ml of
formulation FRII1(a) have been added, then is wrung
under the same conditions as the reserved sample.

20 During the rinse cycle the pH of the medium reaches 7.

After wringing, the articles are placed on a rack to dry.

After drying, a digital color photograph is taken of an area of the dry samples, which is
25 subsequently converted into 256 levels of grey (grey scale from 0 to 255).

The number of pixels corresponding to each level of

grey is counted.

For each resulting histogram the standard deviation σ of the distribution of the level of grey is measured. If wrinkling is substantial, the distribution of the level of grey is large.

σ_1 corresponds to the standard deviation corresponding to the reserved sample (rinsed without a rinsing formulation).

σ_2 corresponds to the standard deviation obtained with the rinsing formulation in question.

σ_3 corresponds to the standard deviation obtained on flat starting samples which have not undergone an operation of washing, rinsing or wringing.

The performance value WR (wrinkle recovery) is given by the following equation

$$WR(\%) = [(\sigma_1 - \sigma_2) / \sigma_1] f \times 100$$

where f is a standardization factor, equal to $1 / [(\sigma_1 - \sigma_3) / \sigma_1]$

A value of:

- 0% corresponds to zero benefit.
- 100% corresponds to a flat surface

The results of the wrinkle test are as follows:

Rinsing formulation	FR	FRII(a)	FRIII(a)
WR	30%	40%	55%

Easy-iron test

The ease of ironing is evaluated by comparison with the ironing of the sample placed in reserve (rinsed without

formulation, wrung and dried).

The values given have the following signification:

0 signifies that there is no perceptible difference

- 5 1 signifies that ironing is slightly easier
 2 signifies that ironing is markedly easier
 3 signifies that ironing is very much easier
 to an even greater extent

The results obtained are as follows:

Rinsing formulation	FR	FRI1(a)	FRII1(a)
Ease of ironing	1	2	3
Hand	Soft	Silky	Very silky

- 10 The hand of the treated samples was also evaluated by a group of testers. The results are given in the table above.

The above results show that the addition of the vehicle (V) enhances the deposition of the active
 15 substance (A) on the fabric, which is manifested in an improvement in the antiwrinkle effect of the active substance (A).

Example 2: Soil release effect

Formulation I2

- 20 Use is made of a cationic aqueous dispersion (latex) of a poly-tert-butyl acrylate, having a particle size of 45 nm, obtained by emulsion polymerization in the presence of 10% by weight of surfactant Dehyquart ACA. The dispersion has a dry extract of 30% by weight.

The units derived from the tert-butyl acrylate are capable of undergoing hydrolysis at basic pH, giving rise to acrylic functions in sufficient quantity to make the polymer swell at the pH of the rinsing medium
5 and to make it soluble at the pH of the subsequent washing medium.

Under mechanical stirring, 20 ml of the dispersion are poured into 1 ml of water whose pH has been adjusted to 4.5.

10 2 g of sodium chloride are added (for better comparison with formula II2 below).

Formulation II2

Use is made of a cationic aqueous dispersion (latex) of a poly-tert-butyl acrylate, having a particle size of
15 45 nm, obtained by emulsion polymerization in the presence of 10% by weight of surfactant Dehyquart® ACA. The dispersion has a dry extract of 30% by weight. Also prepared is a 1% by weight solution of carboxymethylguar which has a degree of substitution of
20 0.04 and a molar mass by weight of 100 000 g/mol, in water whose pH is 4.5.

Under mechanical stirring, 20 ml of the dispersion are poured into 1 ml of the carboxymethylguar solution.

2 g of sodium chloride are added to stabilize the
25 dispersion over time.

Test

The test is carried out in a Tergotometer

laboratory apparatus, which is well known to the formulators of detergent compositions. The apparatus simulates the mechanical and thermal effects of the American-type washing machines with a pulsing action; by virtue of the presence of 6 washing pots, it allows series of simultaneous tests to be carried out with a considerable time saving.

The composition of the laundry detergent employed is as follows:

Composition of the laundry detergent	Parts by weight
Zeolite 4A	25
Light carbonate	15
Disilicate R2A	5
Acrylic/maleic copolymer Sokalan CP5 (BASF)	5
Na sulfate	9.5
Carboxymethylcellulose	1
Perborate monohydrate	15
Tetraacetylenediamine	5
Linear dodecylbenzenesulfonate	6
Synperonic A3 (C12-C15 fatty alcohol ethoxylated with 3 EO)	3
Synperonic A9 (C12-C15 fatty alcohol ethoxylated with 9 EO)	9
Enzyme Esperase 4.0 T	0.5
Fragrances	1

10 The following three rinsing formulations are tested:

* 8 ml of a commercial softener formulation FR
containing only cationic surfactants (15% solids)

* a softener formulation FRI2 consisting of 1 ml of the
formulation FI2 above,

5 * a softener formulation FRII2 consisting of 1 ml of
the formulation FII2 above.

(a) Prewash/rinsing/drying:

3 test specimens measuring 10 x 10 cm and made of flat
woven cotton and 3 polyester test specimens measuring
10 15 x 15 cm are prewashed in a Tergotometer for
20 minutes at 23°C with the above laundering formula;
the water used has a hardness of 30°HT (diluted
Contrexéville® mineral water); the amount of laundry
detergent employed is 5 g per liter of water; the
15 number of test specimens per pot is 6.

The squares of fabric are subsequently rinsed 3 times
for 5 minutes (each time), twice with cold water and
the third time with cold water to which either 8 ml of
commercial rinsing formula FR or 1 ml of the rinsing
20 formulas FRI2 or FRII2 have been added.

The squares of fabric are subsequently wrung out and
then dried on clotheshorses.

(b) Staining:

4 drops of dirty motor oil (DMO) are deposited on the
25 test specimens prewashed as above.

To ensure good fixing of the stains, the soiled fabrics
are placed in an oven at 60°C for 1 hour.

To allow effective reproducibility of the results, the fabrics are washed within 24 hours.

(c) Washing/rinsing/drying:

The soiled tests specimens are washed, rinsed, wrung
5 and dried under the same conditions as those described
in (a).

Evaluation

The reflectance of the fabrics before and after washing
is measured using a Dr. Lange/Luci 100 colorimeter.

10 The efficacy of the test polymer as a soil release
agent is evaluated by the percentage elimination of the
stains, calculated by the formula

$$E \text{ in } \% = 100 \times (R3 - R2) / (R1 - R2)$$

where

15 R1 represents the reflectance before washing of the
unsoiled fabric (step (a))

R2 represents the reflectance before washing of the
soiled fabric (steps (a) and (b))

R3 represents the reflectance after washing of the
20 soiled fabric (steps (a), (b) and (c))

For each test product the mean percentage stain
elimination is calculated.

The results obtained are as follows:

Rinsing formulation	Cotton	Polyester
	E in %	E in %
FR	55	5

FRI2	60	25
FRII2	70	50

Example 3: Fragrance retention

Formulation FI3

1.5% of fragrance are added to 21 ml of an aqueous solution containing 3% of its weight of Dehyquart[®] ACA; the mixture is homogenized on the Ultraturrax. 2 g of sodium chloride are added (for better comparison with formula FIII3 below).

10 Formulation FII3

Use is made of an aqueous dispersion (latex) of a polybutyl acrylate (active substance A) having a particle size of 55 nm, containing 5% by weight of fragrance (organic active substance MAO), obtained by emulsion polymerization of butyl acrylate in which the fragrance was dissolved beforehand (3 parts by weight of fragrance per 100 parts by weight of butyl acrylate), in the presence of 10 parts by weight of Dehyquart[®] ACA (surfactant TAC) per 100 parts by weight of butyl acrylate.

The dispersion has a dry extract of 30% by weight; the Tg of the polymer is -50°C.

20 ml of the dispersion of active substance (A) is poured into 1 ml of water whose pH is 3.

25 2 g of sodium chloride are added (for better comparison

with formula FIII3 below).

Formulation FIII3

Use is made of an aqueous dispersion (latex) of a
5 polybutyl acrylate (active substance A) having a
particle size of 55 nm, containing 5% by weight of
fragrance (organic active substance MAO), obtained by
emulsion polymerization of butyl acrylate in which the
fragrance was dissolved beforehand (3 parts by weight
10 of fragrance per 100 parts by weight of butyl
acrylate), in the presence of 10 parts by weight of
Dehyquart® ACA (surfactant TAC) per 100 parts by weight
of butyl acrylate.

The dispersion has a dry extract of 30% by weight; the
15 Tg of the polymer is -50°C.

Also prepared is a 1% by weight aqueous solution of
xanthan gum (Rhodopol® T from Rhodia) in water whose pH
is 3.

20 ml of the dispersion of active substance (A) is
20 poured into 1 ml of the xanthan gum solution, vehicle
(V), under mechanical stirring.

2 g of sodium chloride are added in order to enhance
the stability of the dispersion.

25 These three formulations contain 1.5% by weight of
fragrance; they are odorant.

Testing

Prewash/rinse/drying:

3 cotton test specimens measuring 6 × 6 cm,
3 polyester/cotton blend test specimens measuring
5 6 × 6 cm, and 3 polyester blend test specimens
measuring 6 × 6 cm are introduced into each pot of a
Tergometer and prewashed for 20 minutes at 40°C with a
commercial laundry detergent formula; the water used
has a hardness of 30°HT (diluted Contrexéville® mineral
10 water); the amount of detergent employed is 5 g per
liter of water.

The squares of fabric are then rinsed 3 times for 5
minutes (each time); two of these rinses are with cold
water; the third rinse is with mains water, and 1 ml of
15 formulations FI3, FII3 and FIII3 above are added to
each of the pots.

The squares of fabric are subsequently wrung out then
dried on a frame in the open air.

Testers score from 0 to 10 the intensity of the
20 fragrance on the fabrics after 1, 3, 7, and 10 days of
storage of the fabrics in the open air.

The values given have the following signification:

- . 0 signifies that there is no perceptible odor
- . 10 signifies that the odor is peristent

25 The results obtained are as follows:

Odorous intensity			
Storage period	Formulation		
	FI3	FII3	FIII3
1 day	5	7	8
3 days	0	5	7
7 days	0	3	5
10 days	0	1	4

On the one hand these results show that

- when the fragrance is not in "encapsulated" form in the active substance (A) its odor on the fabrics is not maintained (formulation FI3)
- when the fragrance is in "encapsulated" form in the active substance (A) its odor on the fabrics is maintained (formulations FII3 and FIII3).

10

On the other hand, and this is the subject matter of the invention, a comparison of the results obtained with formulations FII3 [active substance (A)

"encapsulating" the fragrance in the absence of vehicle (V)] and FIII3 [active substance (A) "encapsulating" the fragrance in the presence of vehicle (V)] shows that the improvement observed with formulation FIII3 is due to the fact that the amount of active substance (A) "encapsulating" the fragrance, deposited on the fabric,

is greater than with formulation FII3, which does not contain vehicle.